Computational Study of Nanometer-Scale Self-Propulsion

Enabled by Asymmetric Chemical Catalysis

Yunfeng Shi,1 Liping Huang1 and Donald W. Brenner2

1Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180

2Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695-7907

Abstract

We present a detailed analysis of the self-propulsion of a model nanometer-scale motor by reactive molecular dynamics simulations. The nanomotor is decorated with catalysts on only one side that promotes exothermic reactions of the surrounding fuel. Unidirectional drift of the nanomotor is observed that is superimposed on its Brownian motion. The motor response upon the application of external loads is also investigated and the thermodynamic efficiency is calculated. It is shown that the propulsion of our nanomotor can be understood by a momentum transfer model which is akin to rocket propulsion.

Keywords: molecular motor, catalyst, molecular dynamics, autonomous motion, momentum transfer.
I. Introduction

A continuing challenge for nanometer-scale science and technology is to create self-propelling systems that are capable of providing mechanical work at high efficiency.\textsuperscript{1,2,3} Such systems hold promise for a wide range of applications that include directed self-assembly, drug delivery, nanofluidic and nanorobotic systems. A major inspiration for this endeavor comes from biomolecular motors that function in synthesis, transportation and actuation processes in biological systems.\textsuperscript{4} A natural strategy is to directly incorporate biomolecular motors with inorganic materials into hybrid nanodevices,\textsuperscript{5} or utilize biological building blocks to generate motion.\textsuperscript{6,7,8,9,10} However, these approaches are limited by the working environment and fuel type, as required by the biological components. For non-biological systems, controlled motion has been observed in systems that include supramolecules,\textsuperscript{1} metal nanocrystal devices\textsuperscript{11} and magnetic colloidal chains.\textsuperscript{12} The operation of these motors is mostly powered by an external agitation such as light, an electric/magnetic field or oscillating chemical concentration. Therefore, unlike biomolecular motors, the motions of the above artificial motors are not strictly autonomous.

Recently, it has been shown that catalytic bimetallic nanorods exhibit interesting self-propelled motion in hydrogen peroxide solutions.\textsuperscript{13,14,15,16,17,18,19,20} These nanorods have comparable size, speed and energy source (catalytic chemical reactions) to bacteria. The original approach has been expanded to systems with alternative motors (consisting of polymer\textsuperscript{21} or silicon\textsuperscript{22}), fuels (hydrazine\textsuperscript{23} or glucose\textsuperscript{24}) and catalysts (synthetic molecular catalysts\textsuperscript{25} or enzymes\textsuperscript{24}). Various propulsion mechanisms have been put forth, including bubble recoil,\textsuperscript{13,14,20,22} interfacial tension,\textsuperscript{15} self-electrophoresis,\textsuperscript{16,18} self-diffusiophoresis.\textsuperscript{21,26,27} The precise origin of the driving force is thought to be system-dependent and multiple propulsion
mechanisms might operate at the same time. For instance, self-electrophoresis seems to be responsible for propulsion in bimetallic nanorod systems, while self-diffusiophoresis is likely to play an important role for systems without electrochemical reactions. An apparent universal feature is to achieve asymmetric reactions by placing the catalysts on one side of the motor or partially blocking the release routes of the products. One exception is the recent demonstration of the self-propelled motion of a single-component nanorod without the bimetallic structure to break the symmetry. Instead, it is perceived that the necessary asymmetry is due to the oblique inclination of the nanorods to the buoyancy/gravitational direction.

The smallest dimension of the catalytic molecular motors investigated in the above studies is about one third of a micron. This is largely due to the technical difficulty in discerning directional motion for objects at submicron sizes. Therefore it is unclear whether this type of catalytic system can operate when being scaled down to the tens of nanometers (or less) scale. In addition, the thermodynamic efficiency of catalytic molecular motors has not been directly measured. By considering the viscous drag force instead of coupling external loads, Paxton et. al. estimated the efficiency of bimetallic nanorods to be on the order of $10^{-9}$. Although it is possible to enhance the efficiency by 8 times through incorporation of carbon nanotubes into the catalytic end, the motor efficiency is still extremely low. The fact that multiple (sometimes competing) propulsion mechanisms operate simultaneously makes it difficult to rationally optimize these nanomotors.

On the other hand, theoretical investigations on molecular motors have focused on either complicated biomolecular motor systems or idealized Brownian motors. There is very little simulation work to understand catalytic molecular motor systems that use asymmetric catalytic reactions. Ruckner, Tao and Kapral studied a self-propelled catalytic-inert nanodimer
using a hybrid mesoscopic-molecular dynamics scheme. They observed directional motion of the nanodimer that originates from concentration gradients as well as unequal affinities to the solution. However, the catalytic reaction was implemented by Monte Carlo operations so that the estimation of chemical energy expense is not straightforward and the motor efficiency was not determined. Cordova-Figueroa and Brady studied osmotic propulsion as a result of chemical reactions using Brownian dynamics simulations. Questions remain whether entropic-mixing is sufficient for propulsion. It was suggested that exothermic reaction has to be explicitly modeled in any theoretical modeling to understand chemically propelled autonomous motion.

In this paper we present a detailed theoretical investigation of a nanometer-scale motor propelled by asymmetric chemical catalysis within a surrounding fuel environment. Instead of focusing on a particular experimental catalytic nanomotor, the objective of this work is to examine the generic dynamics of reaction-induced propulsion at the molecular level. Autonomous motion, which is simulated by reactive molecular dynamics (MD) trajectories, is observed at the nanoscale. The effects of temperature, motor construction and simulation constraints on the free drifting behavior are also investigated. Furthermore, the nanomotor is subjected to external force opposite to the self-propelled direction. With the precise knowledge of the extent of chemical reactions, the thermodynamic efficiency of the motor at different load is calculated. Finally, a propulsion mechanism based on momentum transfer is formulated that agrees with the MD simulation results.

II. Reactive state summation fuel-catalyst force field

Rather than attempting to model a specific system, we have chosen to model a generic asymmetric fuel-catalyst system using a reactive interatomic potential. The advantages of this
approach, as opposed to quantum mechanical calculations or highly-accurate empirical force field (such as REBO\textsuperscript{39,40,41} and ReaxFF\textsuperscript{42,43}), are moderate computational demands which allow us to attain statistically significant results and generalizable observations. By utilizing reactive molecular dynamics simulations, the hydrodynamic dragging force, exothermicity of the reaction and various energy transfer processes, which all affect the unidirectional drift of the molecular motor, can be described simultaneously.

Based on the reactive state summation (RSS) empirical potential,\textsuperscript{44} a model fuel-catalyst force field was devised for this study. The central strategy in the RSS scheme is to combine non-reactive force fields that are modulated by many-body weighting function. The weight function depends on a reaction coordinate. The attractive features of the RSS scheme include flexibility, expandability and computational simplicity. This scheme has been used to study the detonation behavior of nitrogen cubane,\textsuperscript{44,45,46} the growth of nanoporous carbon,\textsuperscript{47} and the phase transformation of silica\textsuperscript{48} and boron oxide.\textsuperscript{49}

II.A Formulation

The model fuel-catalyst system consists of three types of atoms: fuel atom (F), catalyst atom (C) and inert atom (I). These atom species are generic models and do not correspond to particular chemical elements. The chemical reaction of the primary interest is the combination reaction of monatomic fuel molecules (as reactants) to diatomic fuel molecules (as products). The goals in the formulation and parameterization of the force field are: (1) the combination reaction of the fuel atoms without catalysts is exothermic and with a relatively high reaction barrier; (2) the combination reaction of the fuel atoms, in the vicinity of the catalyst, is exothermic and with a relatively low reaction barrier. The inert atom is hard-sphere like and does
not participate in chemical reactions. The force field is constructed in the following manner.

More details can be found in Ref. [44]. First, interatomic forces for each reactive state, including the reactant and product, are described by conventional two-body interactions. A reactive coordinate is then given as a function of atomic species via the Kronecker delta function and the local environment. Thus, the many-body effects, which are essential for covalent bonding, are introduced in a reactive-coordinate-dependent weight function. Finally, the total potential energy of the whole system is the sum of individual potentials for each reactive state modulated by a weighting function:

\[
PE = \frac{1}{2} \sum_{i \in N} \sum_{j \neq i} \left( \sum_{s} \delta(t_i, t^*_i) \delta(t_j, t^*_j) w_i E^s(r_{ij}) \right)
\]  

where \(i, j\) loops over \(N\) atoms, \(s\) loops over the reactive states including any number of reactants, products and intermediates. \(\delta\) is the Kronecker delta function that nullifies the contribution from reactive state \(s\), unless the atom types of \(i\) and \(j\) (denoted \(t_i, t^*_i\)) match \(t^*_1\) and \(t^*_2\). \(E^s(r_{ij})\) is the pair potential for reactive state \(s\). The weighting function \(w_i\) is written as:

\[
w_i = e^{-A_1-CN_i-CN_j-A_2-CN_i-CN_j-A_3-CN_i-CN_j} \tag{2}
\]

\[
CN_{i,F} = \sum_{j \neq i} \delta(t_j, F) f_{CN}(r_{ij}) \tag{3}
\]

\[
CN_{i,C} = \sum_{j \neq i} \delta(t_j, C) f_{CN}(r_{ij}) \tag{4}
\]

\[
CN_i = \sum_{j \neq i} f_{CN}(r_{ij}) \tag{5}
\]

\[
f_{CN}(r_{ij}) = \begin{cases} 
1 & r_{ij} \leq r_{ij}^c - 2w \\
\frac{1}{2} + \frac{1}{2} \cos \left[ \frac{\pi}{2} \left( \frac{r_{ij} - r_{ij}^c + w}{w} \right) + 1 \right] & r_{ij}^c - 2w < r_{ij} < r_{ij}^c \\
0 & r_{ij} \geq r_{ij}^c \end{cases} \tag{6}
\]
The reactive state is specified in terms of the total coordination number $CN$, partial coordination number $CN_F$ (counts only fuel atoms) and partial coordination number $CN_C$ (counts only the catalyst atoms). Therefore, the weight function calculates the difference between those specified for this particular reactive state ($CN$, $CN_F$ and $CN_C$) and those calculated instantaneously for each atom ($CN$, $CN_F$ and $CN_C$). The parameters $A_F$, $A_T$ and $A_C$ define the selectivity of this reactive state or the phase space it covers. That is, for a very large $A$ value, the weight function is zero unless the reactive states match exactly; for a zero $A$ value, the particular reactive state is insensitive to the reactive state and contributes to the total force field very much like a two-body interaction. The coordination numbers are calculated as the sums of a neighbor-counting function $f_{CN}$ as in Equation (6). $f_{CN}$ is a smooth function changing from 1 to 0 in a transition region of width $2w$ from $r_{ij}^c - 2w$ to $r_{ij}^c$ as the interatomic distance increases.

Ten reactive states are included in Equation (1). The functional forms as well as the parameters are listed in Table 1. Those parameters are chosen such that: (1) all the atoms have an equal mass of $3.32 \times 10^{-26}$ kg (20 amu); (2) the equilibrium separation for the diatomic product molecule is 0.3 nm; (3) the exothermicity at 0 K of the combination reaction of the fuel atoms equals that of the hydrogenation reaction of formaldehyde to methanol (85.3 kJ/mol \(^{50}\)). Therefore, after the mass, length and energy scale are defined, all other physical quantities can be consequently determined in SI units.

We use three types of interatomic potential for $E'(r_{ij})$ to describe the bonded interactions as well as the non-bonded interactions. The first one is a two-body Morse-type potential that is used in the first four reactive states (state 1 through 4):

$$E^{Morse}(r_{ij}) = \xi (e^{2\rho I_1 \sigma - r_{ij}} - 2e^{\rho I_1 \sigma - r_{ij}}) f_{cutoff}(r_{ij}) \quad (7)$$
\[ f_{\text{cutoff}}(r_{ij}) = f_{\text{CN}}(r_{ij})^B \]  
(8)

The second type for \( E^r \) is a hard sphere (HS) form that is used in reactive states 5 and 6:

\[
E_{\text{HS}}^r(r_{ij}) = \begin{cases} 
\varepsilon \cdot e^{\sigma R_{ij} / r_{ij}} & r_{ij} < R_c \\
0 & r_{ij} \geq R_c 
\end{cases}
\]  
(9)

The third type for \( E^r \) is a truncated and shifted Lennard-Jones potential that is used in the rest of the reactive states:

\[
E_{\text{LJ}}^r(r_{ij}) = 4\varepsilon \left[ \left( \sigma / r_{ij} \right)^6 - \left( \sigma / r_{ij} \right)^{12} \right] - 4\varepsilon \left[ \left( \sigma / R_c \right)^6 - \left( \sigma / R_c \right)^{12} \right]
\]  
(10)

The role of each individual reactive state is as follows. Note that each state is restricted to particular pairs of species. The first two reactive states concern the interaction between two fuel atoms. Reactive state 1, a conventional Morse term, provides the potential well for the diatomic product molecule. Reactive state 2, on the other hand, has a negative \( \varepsilon \) parameter which provides a non-zero barrier for the combination of two fuel atoms. The combined effect of reactive state 1 and 2 is a positive energy barrier in front of the normal potential well, as can be seen from Figure 1(a). As two isolated fuel atoms approach each other, a reaction barrier has to be overcome before a diatomic product molecule forms with heat release. The next two reactive states (3 and 4) deal with the interaction between one fuel and one catalyst atom. Reactive state 4, which is analogous to reactive state 1 in the fuel-fuel interaction, provides the potential well for the fuel-catalyst interaction. Similarly, reactive state 3, which is analogous to reactive state 2, produces a reaction barrier for the combination of fuel-catalyst. The combined effect of reactive states 3 and 4 can be seen from Figure 1(b). The catalytic effect occurs because both reactive state 2 and 3 are total-coordination-dependent. That is, any deviation from a total coordination of 1 diminishes the contribution of reactive states 2 and 3, which both provide the positive barriers. Therefore the
reaction barrier of the combination of two fuel atoms is lower in the vicinity of another atom. Catalyst atom is more effective because the energy penalty for the intermediate separation is lower (as shown in Figure 1) thus a catalyst is more likely to be adjacent to a fuel atom.

Reactive state 5 deals with the three-atom complex (C-F-F) in which one catalyst atom and two fuel atoms are mutually bonded. The potential energy of this complex has to be higher than that of an F-F pair (product) plus an isolated catalyst atom, so that the removal of a catalyst atom from the C-F-F complex is energetically favored. The pair potential in reactive state 5 is purely repulsive and its weight function strictly selects this intermediate state (C-F-F). Therefore, reactive state 5 effectively increases the potential energy of the three-atom complex to provide the driving force for the removal of the catalyst atom.

Reactive state 6 prevents overlapping of atoms regardless of their reactive states. The weight functions of reactive state 7 to 12 are all unity. Therefore these terms describe Van der Waals interactions and do not affect breaking or forming of covalent bonds. All Van der Waals interactions are repulsive except for the catalyst-inert and inert-inert interactions, which are important for the stability of the inert crystal and the adsorption of catalysts on the inert crystal, as in the unconstrained nanomotor model (Section III.E).

II.B Reaction path analysis by nudged elastic band method

To understand the catalytic reaction mechanism for the RSS fuel-catalyst force field, the combination reaction of two fuel atoms at the presence of one catalyst atom in a collinear geometry is studied using the nudged elastic band (NEB) method. The central atom is a fuel atom with one catalyst atom and a second fuel atom on each side. The potential energy landscape is shown in Figure 2, where the two independent degrees of freedom are the distance from the
central atom to the catalyst atom ($r_{FC}$) and to the other fuel atom ($r_{F}$). The start and end point for the NEB method are points A and D, respectively. Point A represents the configuration that all three atoms are far away from each other, while point D represents the configuration that two fuel atoms bond to each other (a diatomic product forms) with the catalyst far away. The reaction path revealed by the NEB method involves three steps as shown in Figure 2: (1) the center fuel atom first binds to the catalyst (A to B); (2) the other fuel atom starts to approach the center fuel atom so that the central atom bonds to both the catalyst and the fuel atoms (B to C); (3) the catalyst atom moves away and a diatomic product molecule is left (C to D).

As seen in Figure 3, the reaction barriers for the above three-step catalytic reactions are 0.0453, 0.142 and 0.13 eV, respectively. In comparison, the reaction barrier for the direct combination of two fuel atoms without the presence of catalyst atoms is 0.40 eV. The path of this direct combination reaction is also shown in both Figure 2 and Figure 3. It is clear that the catalyst lowers the reaction barrier of the combination reaction substantially. We have also carried out the same analysis on geometries in which the three atoms are not collinear. It was found that the reaction barrier remains the same for small deviations of the C-F-F angle away from 180 degrees and increases for large deviations.

Without catalysts, the presence of a third fuel atom also lowers the barrier of the combination reaction of two fuel atoms into products to 0.31 eV. Therefore, the fuel atom itself can act as a catalyst. It can also be shown that a cluster of fuel atoms is capable of lowering the reaction barrier even more. However, this self-catalytic effect from fuel atoms is not as effective as the catalyst atom, as reflected in the reaction rates described in the next section.

II.C Reaction rate
The above analysis of the potential energy landscape is very useful to comprehend the intended catalytic effect. However, the existence of the reaction path ABCD (with a lower reaction barrier as opposed to the original reaction path) does not guarantee a significantly enhanced reaction rate. To include kinetic effects, we compared the reaction rates of fuels with or without catalysts using molecular dynamics simulations. The first simulation system contains 112500 fuel atoms and 12500 catalyst atoms. The second simulation system contains 112500 fuel atoms and 12500 inert atoms. The size of both simulation systems is $58.5 \times 58.5 \times 58.5$ nm$^3$. The number density of the fuel is $5.62 \times 10^{26}$ m$^{-3}$, which is very close to that of the nanomotor system as described later. At time zero in both systems, atomic positions are randomized and atomic velocities are thermalized to a prescribed initial temperature. The simulation is then run at constant volume and energy. During the simulations, diatomic fuel molecules are formed depending on the temperature, concentration of fuel and whether the catalyst is present. The reaction rate can be extracted by tracking the population of products as a function of time. We consider a fuel atom to be a product if it has a neighboring fuel atom within 0.375 nm (the upper bound of the first peak of the radial distribution function for the products). The reaction rate can be calculated as the slope of the linear fitting of the products vs. time. Such estimation of reaction rate is only accurate when the temperature and the fuel concentration are constants. However, because the total energy of the system is conserved and the combination reaction of the fuels is exothermic, the temperature increases slightly as reaction proceeds. Moreover, the fuel concentration also decreases during the process. To minimize these effects, the simulation time is chosen to be between 8.63 (for high temperatures) to 43.2 ps (for low temperatures) to ensure the extent of reaction is minute. In this way, for all simulations, the temperature increases by less than 10% and the fuel concentration decreases by less than 1%.
The Arrhenius plot of reaction rates as a function of temperatures is shown in Figure 4. The apparent activation energy for the fuel combination reaction is 0.08 eV with catalyst and 0.135 eV without catalysts; i.e. the presence of the catalyst atoms lowers the activation energy by about two fifths. The activation energy from the Arrhenius plot is different from the reaction barriers obtained from the NEB method. This is because the reaction barriers from the NEB method are for three-atom systems while multi-atom clusters contribute to the reaction in the MD simulations. Moreover, the prefactor in the Arrhenius relation is temperature-dependent. The catalytic effect is more pronounced at low temperatures. For instance, at 116 K, the reaction rate increases 70-fold at the presence of catalyst. However, at 174 K, the enhancement of reaction rate is only 10-fold.

III. Simulation results for molecular motors

III.A Simulation system setup

The size of the simulation box (Figure 5) is 18×60×18 nm³. The simulation system is periodic in all three directions. A rectangular motor (9×6×9 nm³) is positioned inside the system that is aligned with the simulation box. The motor occupies about 1/4 of the cross-section of the whole simulation system. To investigate system size effects, systems which are twice as large in both the X- and Z-direction were simulated and almost identical results compared to the smaller systems were obtained. A total of 75 catalyst atoms are packed in a simple cubic lattice with a spacing of 1.8 nm. This spacing is sufficiently large (almost three times the cut off distance of the reactive force field) so that the catalytic effect of one catalyst will not be affected by its neighbor catalyst atoms. There are also 865 inert atoms in the motor constituting the motor wall. A single layer of inert atoms covers the catalyst in all faces of the motor except the
negative Y face. The inert atoms are also packed in a simple cubic lattice with a spacing of 0.6 nm. The inert layer is dense enough that neither the monatomic fuel nor diatomic product molecules can pass through. The velocities of the catalyst and inert atoms are set to zero in the initial configuration. There are a total of 10683 fuel atoms with random positions inside the simulation box excluding the volume that is occupied by the motor. The number density of the fuel is $5.56 \times 10^{36} \text{ m}^{-3}$. The velocities of the fuel atoms at time zero are determined according to the initial temperature.

Classical equations of motion for the atoms are numerically integrated without temperature or pressure control with a time step of 0.173 fs. The advantage of using a microcanonical ensemble, as opposed to coupling to a thermostat, is that mass, momentum and energy are conserved locally so that the correct hydrodynamics emerge naturally. Furthermore, the dynamics of the chemical reaction will not be perturbed by the introduction of the thermostat. The disadvantage is that the varying temperature of the system due to the exothermic chemical reactions which complicates the analysis. Simulations in which the systems are coupled to a Nose-Hoover thermostat\textsuperscript{53,54} have also been carried out to control the system temperature. Similar results are obtained in those simulations in which catalytic chemical reactions propel the spontaneous motions.

There are two additional constraints applied to the system which are very similar to Ref.\textsuperscript{55} The first constraint is that the coordinates for each of the catalyst and inert atoms are not updated according to their individual forces and velocities. Instead, the total force and velocity of the whole motor is used so that the motor (including the inert and catalyst atoms) behaves like a rigid body. Thus the motor is somewhat analogous to a solid porous medium dispersed with catalysts. The second constraint is that the total force of the motor in the X- and Z-direction is set
to zero. Thus the motor is bound to move only along the Y-direction (constrained on a virtual track). The second constraint can be realized experimentally, for example, by confining a shuttling nano-ring along a carbon nanotube. It should be noted that the observed spontaneous motion of the motor is not a result of the two constraints described above. They are used solely to speed up the computation and simplify the analysis. Further discussions regarding the constraints will be given in Section III.E.

III.B Spontaneous motion of the nanomotor

The nanomotor as described in the proceeding section is released in a fuel environment with an initial temperature of 116 K. Five independent simulations were carried out to reduce sample-to-sample variations. Figure 6 shows the lower edge of the nanomotor as a function of time for all five simulations. Because the motor is free of fuel atoms at time zero, the nanomotor experiences a negative total force (pushing down) primarily from the fuel gas above it. Consequently, the motor moves down initially. After a short period of time, the fuel atoms fill in the motor from below to balance the pressure from above. Figure 6 shows that the motor starts to move up after about 86 ps. This motion is best characterized as a small directional motion superimposed on a Brownian motion. The velocity of the upward motion is 5.6 m/s. The velocity of the random motion can be characterized by a temperature that is equal to that of the surrounding fuel atoms. This is illustrated in the inset of Figure 6.

As the nanomotor moves up, the catalyst atoms inside the motor continue to catalyze the combination reaction of the fuel atoms. As expected, the majority of the reactions occur inside the motor as shown in Figure 7. However, there are small amount of diatomic product molecules formed outside the motor via reaction routes that do not involve catalyst atoms. It is also worth
noting that the reaction rate increases continuously as the simulation proceeds as shown in Figure 7. This is because the system temperature increases due to the exothermic chemical reaction.

The catalytic chemical reactions produce both thermal and concentration gradients near the opening of the motor as shown in Figure 8. Because those two distributions are quite similar, only the kinetic energy distribution will be discussed. Due to the geometry of the motor, it is interesting to compare the thermal energy distribution in regions within the X-Z projection of the motor (solid lines) and those outside (broken lines) in Figure 8. The peak of the kinetic energy distribution within the projection of the motor locates inside the motor. However, the peak of the kinetic energy distribution outside the motor projection, which is much smaller, is located below the opening of the motor. For regions far enough from the motor, these two distributions overlap due to sufficient thermal diffusion. As expected, the heat generated inside the motor flows primarily in the negative Y-direction because the hot products can only exit through the bottom opening of the motor. As a result, the bottom of the motor is significantly hotter than the top of the motor. Also as shown in Figure 8, the thermal gradient increases as a function of time due to the elevated chemical reaction rate.

The asymmetric chemical reaction on two sides of the motor wall leads to heat and product accumulation below the motor (as shown in Figure 8). However, the phoresis effect from this concentration or temperature gradient is minimal because the side walls of the motor are repulsive-only and atomically flat. Therefore there is no interfacial layer structure formed, that is vital for phoretic transport for colloidal particles. Instead, the upward motion of the motor is a result of the exhaustion of the hot product through the bottom. A propulsion model based on momentum transfer is given in Section IV.B.
III.C Chemically-driven motion at different temperature

To correlate the motor motion to chemical reactions, the initial temperature of the fuel is set from 29.1 to 174 K. For each initial temperature, five independent simulations were carried out. The displacements of motors for various initial temperatures are plotted in the top pane of Figure 9. The amounts of products are plotted for comparison in the bottom pane. There exists a strong correlation between spontaneous motion and chemical reactions. For initial temperatures below 72.6 K, there is neither chemical reaction nor motor motion. For initial temperatures above 87.0 K, the displacement increases with the initial temperature because the reaction rate is strongly temperature-dependent. However, for temperatures higher than 131 K, the displacement decreases slightly as temperature increases. This is mainly because at high temperatures the catalytic effect diminishes.

III.D Design consideration for the motor

Based on the nanomotor described in section III.A, two variations are applied to illustrate the essential ingredients in nanomotor design. For the first variation, the catalyst atoms inside the motors are removed so that no catalytic reaction occurs. For the second set, the upper inert layers are removed (both ends of the motor in the Y-direction are open) with the catalyst atoms present. Consequently, the catalytic reactions are symmetric. The simulation conditions are otherwise identical to those in section III.B. Five independent simulations were carried out to obtain sample-to-sample variations for both cases. The net displacements are $0.6 \pm 0.2$ and $-1.0 \pm 0.6$ nm for the above sets of simulations, respectively. In comparison, the net displacement of the original motor is $9.5 \pm 0.4$ nm. Therefore, both the presence of catalysts and asymmetric opening design are critical to the spontaneous motion of the motor.
III.E The effect of constraints on the locomotion

There are two constraints imposed in all the nanomotor simulations above. The first one is to hold the nanomotor rigid. The second one is to restrict its motion only along the Y-direction. Both constraints affect the energy transfer from the catalytic reactions to motor motion by preventing energy dissipation modes such as spinning and lattice heating of the motor wall. Here we try to understand whether these dissipation modes, if allowed, can significantly reduce the drifting velocity or even destroy the autonomous motion completely.

The original motor wall is replaced by an inert solid with a hollow inside and one opening at the negative Y-direction. The atoms in solid are in a face-centered cubic lattice. The shape and dimension of the new wall is the same as the original constrained motor. There are about 10000 inert atoms in the nanomotor (in comparison, the original nanomotor has less than 900 inert atoms). The catalyst atoms (102 catalyst atoms in total) are placed on the inner surface of the nanomotor. Due to the strong interaction between the catalyst atom and the inert wall, the catalyst atoms remain absorbed on the surface during the course of the simulation. The catalyst atoms do diffuse within the inner surface and are often trapped at the corners of the inner surface. The force field remains the same (Table 1).

The unconstrained nanomotor is released in a fuel environment with an initial fuel temperature of 116 K. Five independent simulations were again used to reduce random fluctuations. The average reaction rate is approximately $1.05 \times 10^{-13}$ mol/s, which is about 30% lower than the original system. This is mainly due to the accessibility difference for the catalysts between dispersing on the surface and scattering in three-dimensional space. Therefore the
catalytic effect is less pronounced in the unconstrained nanomotor even though the total number of catalyst atoms is higher.

As shown in Figure 10, the motors move along the same propulsion direction (the surface normal of the upper lid) in addition to rotation and shift. The total distance the nanomotor travels along the driving direction, which is similar to the velocity calculation in Ref. 35, is calculated to be about 2.7 ± 0.4 nm. It is apparent that the autonomous motion is preserved upon the removal of the two constraints.

The drift speed for the unconstrained nanomotors is 1.6 ± 0.3 m/s, which is about one third of the drifting velocity predicted from the propulsion model (section IV.B), based on the measured reaction rate. This is due to various energy dissipation modes (motor rotations, wall heating) which are not considered in the propulsion model.

IV. Motor performance and propulsion mechanism

IV.A Motor efficiency

The simulations performed so far only concern the spontaneous movement of the nanomotor during which no external force acts along the direction of the motion, i.e. there is no energy transfer into or out of the system. Note that the force from the application of the second constraint is perpendicular to the motor motion in the Y-direction. Therefore, it is interesting to investigate the nanomotor motion that is under external force along the direction of motion. More importantly, the motor performance can be evaluated by its motor efficiency from such simulations.

A constant external force ranging from 0.12 to 2.26 pN was applied opposite to the direction of the spontaneous motion. The simulation was otherwise the same as described in
section III.B. There were 20 independent simulations for every value of the external force. The resulting average velocity of the motor as a function of the external force is plotted in Figure 11. The linear relationship between the drift velocity \( v \) and the external force implies that the motor is propelled by a constant driving force \( F_{\text{propulsion}} \) which is balanced by the combination of the external force \( F_{\text{ex}} \) and a friction force from the fuel environment (\( \gamma \) is the drag coefficient):

\[
F_{\text{propulsion}} + F_{\text{ex}} - \gamma v = 0
\]

(11)

Thus,

\[
v = \frac{1}{\gamma} F_{\text{ex}} + \frac{F_{\text{propulsion}}}{\gamma}
\]

(12)

A linear fit yields \( \gamma = 3.15 \times 10^{-13} \) kg/s and the \( F_{\text{propulsion}} = 1.69 \) pN. The pressure from the chemical propulsion is about 2% of the pressure of the unreacted fuel gas. The work done by the motor through the external force during time \( \Delta t \) is,

\[
\Delta W = -F_{\text{ex}} \cdot v \Delta t
\]

(13)

Thus the thermodynamic efficiency of the molecular motor can be calculated as,

\[
\eta = \frac{\Delta W}{k_r \Delta t \cdot \Delta E}
\]

(14)

where \( \Delta E \) is the chemical energy change for one combination reaction of the fuel atoms at 0 K \((0.876 \text{ eV})\) and \( k_r \) is the reaction rate (measured to be \( 1.44 \times 10^{-13} \text{ mol/s} \)) . This is appropriate because in the MD simulations without thermal or pressure control, the change in potential energy goes entirely into the kinetic energy and work to external loads. Substituting the drift velocity using Eq. (12) yields,

\[
\eta = -\beta F_{\text{ex}} (F_{\text{ex}} + F_{\text{propulsion}})
\]

\[
\beta = \frac{1}{\gamma k_r \cdot \Delta E}
\]

(15)
where $\beta$ is calculated to be $-255.8 \text{ nN}^2$. According to Eq. (15), the efficiency is a quadratic function of the external force. Figure 12 shows the measured efficiency values in simulations, which are consistent with those calculated from Eq. (15). The maximum efficiency is

$$\eta_{\text{max}} = \frac{1}{4} \beta F_{\text{propulsion}}^2$$  \hspace{1cm} (16)

under the condition that the external force is equal to one-half of the chemical propulsion. The stall force of the motor is the same as the propulsion force (1.69 pN).

IV.B Propulsion model

The force acting on the motor in the Y-direction comes from the interactions between gas molecules with the upper closed wall, side walls and the catalysts. The first contribution comes from the elastic collisions of the gas molecules on both sides of the upper motor wall. Due to the absence of deformable adsorption layers (flat and repulsive side walls), there is no phoretic force exerted on the side walls of the motor. The third contribution is zero since the interaction between fuels and catalysts (catalytic reactions and collisions) are isotropic. Therefore, the propulsion of the motor comes entirely from the first contribution governed by momentum transfer and can be understood in the same vein as rocket propulsion.

The momentum transfer of the combined system of motor and the gas inside consists of the outgoing flux of hot gas and incoming flux of cold gas through the bottom opening, as well as gas impingement on the upper wall. Complications arise in such a non-equilibrium situation as both the temperature and density of the gas vary with time. Furthermore, the product molecules are mostly not thermalized inside the motor. This can be seen as significant chemical energy release is still stored in the intra-molecular vibration mode after diffusing outside the motor. Because the mean free path of the product molecules inside the motor is approximately half the
depth of the motor, one can assume that the product molecule does not collide with other gas molecules before leaving the motor. One consequence of this assumption is that there will be no thermal energy transfer from the hot products to the gas molecules inside the motor. It should be noted that this “no collision” assumption is strictly valid only in the limit of infinitely dilute fuel gas.

Following the above assumption, the constant chemical propulsion force can be understood in the following physical picture. A product molecule forms in the vicinity of a catalyst atom. Eventually, this product molecule will diffuse out of the motor with or without a collision with the motor wall. If there is a collision between the product and the motor upper-lid, momentum transfer occurs and the motor acquires a certain momentum in the positive \( Y \)-direction. It is the momentum transfer from such collisions that constitutes the chemical propulsion. The impingement of gas molecules without chemical reactions is assumed to be balanced between the two sides of the upper wall. It is further assumed that the entire exothermic energy release goes into intra-molecular vibrations. Therefore the average velocity of a fuel atom in a product molecule along the \( Y \)-direction before colliding is

\[
\bar{v} = \frac{1}{2} \sqrt{\frac{\Delta E / 2}{m_0}}
\]

(17)

where \( \Delta E \) is again the exothermic energy release and \( m_0 \) is the mass of the fuel atom. For an isolated diatomic harmonic oscillator (the rotational and center-of-mass translational kinetic energy are negligible compared to the intra-molecular vibration energy), the time-averaged kinetic energy and potential energy (bond stretching) are equal. Thus the average kinetic energy is \( \Delta E / 2 \) and the average kinetic energy per atom is \( \Delta E / 4 \). The leading \( \frac{1}{2} \) factor in Eq. (17) comes from summing over the projection from all orientations to the positive \( Y \)-direction.
During time $\Delta t$, there are $2k_r\Delta t$ F atoms in products formed, with $k_r$ being the reaction rate.

Approximately half of those products will hit the motor wall while the other half will diffuse out of the motor directly without collision with the upper wall. Because the intra-atomic vibration energy for the diatomic product is much larger than its translational kinetic energy, two atoms in the same molecule have approximately equal and opposite velocities. Therefore, once one atom in a diatomic product molecule collides with the upper wall, the whole molecule will bounce away from the wall so that the other atom will not collide with the wall. Numerical simulations show that, among 80% of all collisions, only one of the two fuel atoms in a product molecule collides with the motor wall. The remaining 20% of collisions do involve both atoms but have a very similar average momentum change per atom. Thus, the impulse on the motor, from below and above, due to collision of the product molecules during $\Delta t$ is:

$$
\Delta I_{\text{below}} = \frac{k_r^{\text{below}}}{2} \Delta t m_0 (2\vec{v} - 2v_{\text{motor}}) 
$$

$$
\Delta I_{\text{above}} = \frac{k_r^{\text{above}}}{2} \Delta t m_0 (-2\vec{v} - 2v_{\text{motor}})
$$

where the velocity of the motor is $v_{\text{motor}}$. Thus the total impulse is

$$
\Delta I = (k_r^{\text{below}} - k_r^{\text{above}}) m_0 \vec{v} \Delta t - (k_r^{\text{below}} + k_r^{\text{above}}) m_0 v_{\text{motor}} \Delta t
$$

In the long time average, the velocity of the motor (no greater than 6 m/s) is much smaller than $\vec{v}$ (about 740 m/s). Therefore the second term of the right-hand side of Eq. (20) can be omitted so that

$$
\Delta I = (k_r^{\text{below}} - k_r^{\text{above}}) m_0 \vec{v} \Delta t
$$
Thus the propulsion force can be calculated in a manner similar to the pressure calculation in the kinetic theory for an ideal gas. By substituting the average velocity in Eq. (17), the total propulsion force is

\[ F_{\text{propulsion}} = \frac{1}{2} (k_r^{\text{below}} - k_r^{\text{above}}) \sqrt{\frac{\Delta E}{2}} m_0 \]  

(22)

The above equation illustrates that the key to obtain propulsion is the asymmetric chemical reaction. If the reaction rate from above (non catalytic reactions) is negligible, we can estimate the propulsion force to be 2.06 pN. This is reasonably close to the value of 1.69 pN obtained from the molecular dynamics simulations.

We can also substitute Eq. (22) into Eq. (16). Again assuming that \( k_r^{\text{above}} \) is small compared to \( k_r^{\text{below}} \), the maximum motor efficiency is

\[ \eta_{\text{max}} = \frac{m_r k_r}{32 \gamma} \]  

(23)

The maximum motor efficiency does not depend on the exothermic energy release but depends on the reaction rate and drag coefficient.

Finally, the free drift velocity can be obtained by substituting the propulsion force using Eq. (22) into Eq. (12) at the condition of zero external force:

\[ v_{\text{drift}} = \frac{1}{2 \gamma} k_r \sqrt{\frac{\Delta E}{2}} m_0 \]  

(24)

The predicted drift velocity is 6.64 m/s which agrees reasonably well with the measured value in simulation (5.6 ± 0.2 m/s). It is worth noting that the drifting velocity due to self-diffusiophoresis is also proportional to the reaction rate.\(^{21,27}\)

IV.C Propulsion at low Reynolds number
One significant difference between the nanomotor model investigated here and the catalytic nanomotors in experiments is the different hydrodynamic regimes to which they belong. The free drifting nanomotor in our simulations has a Reynolds number of about 0.253, while the typical Reynolds number for catalytic nanomotors in experiments is $10^{-4}$. To narrow this gap, we examined the applicability of the current nanomotor design at hydrodynamic regime with a lower Reynolds number. It should be noted that, as limited by molecular dynamics simulations, the lowest Reynolds number that can be achieved here is only around 0.01 which is typical for molecular-level simulations.\textsuperscript{36}

One way to access a lower Reynolds number regime is to decrease the drift velocity while keeping the fuel gas environment as well as the shape of the nanomotor unchanged. Thus the drag coefficient stays the same. According to Eq. (14), the drift velocity is proportional to the reaction rate which in turn depends on the amount of the catalysts. Therefore, one can lower the Reynolds number by decreasing the catalysts inside a nanomotor while maintaining other simulation conditions.

The same nanomotors are constructed as in section III.A except that fewer catalyst atoms are included. Instead of 75 catalyst atoms in the original nanomotor, 25, 9, 4 and 2 catalyst atoms are distributed inside the nanomotors. Simulation conditions are otherwise the same as in section III.B. Ten or twenty independent samples are simulated to acquire sample-to-sample variations. The reaction rate, observed drift velocity, predicted drift velocity from the momentum transfer model as well as the Reynolds number of the nanomotor are listed in Table 2. The propulsion model works very well for systems with Reynolds number as low as 0.01.
V. Discussion

We have modeled an asymmetrically decorated nanomotor in a fuel gas environment. On the one hand, this simulation setup is very similar to catalytic molecular motors using asymmetric reactions. On the other hand, this nanomotor is also related to rocket engines in terms of hydrodynamic behavior and propulsion mechanism. However, important distinctions exist that warrant detailed discussion.

With respect to the autonomous catalytic molecular motors, the viscosity of the fuel gas in the current simulations is about 0.0025 cP (roughly 1/400 of that of water). Consequently, the free-drifting model nanomotor system has a much larger Reynolds number (~ 0.25) than, for instance, that of bimetallic nanorods (~10^{-4}). Although we have shown that this model nanomotor operates in hydrodynamic regime with a Reynolds number as low as 0.01 (Section IV.C), it is still unclear whether the momentum transfer model is valid in an even more viscous environment (Re~10^{-4}). Second, the size of the nanomotor in our simulations is about 10 nm. In experiments, the polymer bead is about 1.6 microns in diameter and the bimetallic nanorod is 2 microns in length. The size of the motor matters because both the total chemical reaction rate and the frictional force are size-dependent. Therefore the motor performance depends sensitively on its dimension. Moreover, gravity, which is believed to be instrumental in propelling micron-sized mono-component rods, plays no role at the nanoscale.

With respect to the analogy to rocket engines, the nanomotor works against viscous dragging force with fuel from the environment, while a rocket engine works mainly against gravity with on-board fuels. The motion of the nanomotor can be characterized by a Brownian motion plus a directional drift while thermal noise is negligible for rocket engines. Moreover, the Reynolds number of the simulation system in this work is much smaller than the onset of
turbulent flow. Therefore the flow around the model nanomotor is laminar while turbulent flow characterizes the hydrodynamic behavior in rocket engines.

It would be also interesting to compare the energy conversion efficiency of the nanomotor in a gas to the catalytic molecular motors in water. We choose the bimetallic nanorod system to compare because the chemical reaction rate is available. Since there are no experimental measurements of the thermodynamic motor efficiency by applying external forces, the Stokes efficiency $^{58}$ is used instead to characterize the motor performance. The Stokes efficiency is $0.00074$ for the model nanomotor and $2.5 \times 10^{-9}$ for the bimetallic nanorod (similar to Paxton’s estimation $^{17}$). Hence, the model molecular motor outperforms the bimetallic nanorod in experiments by five orders of magnitude. The superior performance is largely due to the low viscosity of the gas phase and the high reaction rate. As all existing catalytic molecular motors are studied in water solutions, an apparent way to greatly enhance the motor efficiency is to switch to the gas phase.

The maximum thermodynamic motor efficiency achieved here is about $0.00018$. This efficiency value is still much lower than biomolecular motors or traditional macroscopic motors. The reason is that the chemical energy release during covalent bond formation/breakage is not directly coupled to the motor motion. Instead, the released chemical energy first converts to heat, mostly intra-molecular vibrations, then couples to mechanical work. Thus, most of the chemical energy is lost due to the poor chemo-mechanical coupling. It is believed that a strong coupling, and consequently a high motor efficiency, can be achieved by incorporating proper conformational changes during catalytic reactions, as demonstrated in biomotors.$^{59}$

VI. Conclusions
Motivated by the self-propelled motion of catalytic molecular motors, we studied a minimalist’s catalytic nanomotor immersed in a reactive fuel gas environment. Directional motion is observed and the propulsion can be understood by a simple momentum transfer model. By applying external forces of various magnitudes, the motor efficiency was determined. The Stokes efficiency of the simulated nanomotor is five orders of magnitude higher than that of bimetallic nanorods. The superior performance is largely due to the low viscosity of the gas phase and the high reaction rate.

This nanomotor model constitutes probably the simplest energy conversion nanostructure from chemical energy to mechanical work. This motor design can be rationally improved by utilizing the knowledge of its propulsion mechanism. More sophisticated nanomotors can be designed based on this simple model by incorporating, for instance, conformational changes.

Acknowledgements

We thank Lipeng Sun and Tiegang Fang at the North Carolina State University for stimulating discussions. The molecular dynamics simulations are carried out in LAMMPS. Simulations were performed in the High-Performance Computing Facility at the North Carolina State University and the Computational Center for Nanotechnology Innovations (CCNI) at the Rensselaer Polytechnic Institute.
References


R.D. Johnson, NIST Computational Chemistry Comparison and Benchmark Database (, 2005).


Table 1 Functional forms and parameters for the RSS force field.

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* Denotes all atomic species.
Table 2 Molecular motors with various Reynolds numbers

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<th>Number of samples</th>
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Figure 1
Figure 1. The interaction potential (black lines) of the F-F pair (a) and the F-C pair (b). The contributions from individual reactive states are also plotted.
Figure 2. The potential energy contour of a catalyst atom and two fuel atoms (C-F-F) in a collinear geometry. The two axes correspond to the distance from the central fuel atom to the catalyst atom and to the second fuel atom, respectively. The red dots are the minimum energy path of catalytic combination reaction of fuels obtained from the NEB method. Along the path, the energy minima are states of total isolated atoms (A), one fuel atom bonds to the catalyst atom (B), the central fuel atom bonds to both the catalyst atom and the other fuel atom (C) and one diatomic product with an isolated catalyst atom (D). The green line represents the path of two fuel atoms directly combine without the influence of catalysts. The potential energy is color-coded from pure blue (-1.0 eV) to pure white (0.5eV and above).
Figure 3. The potential energy of the minimal energy path (red line) for the collinear F-C-C reaction from isolated atoms to diatomic product. There are four energy minima along the path for the catalytic reaction which correspond to the four states in Figure 2. The direct combination of two fuel atoms (green line) is also shown.
Figure 4. The Arrhenius plot of the combination reaction of the fuels with or without the presence of catalysts. The temperature is chosen to be the average temperature during each simulation. The solid black lines are the best linear fitting. The error bars represent the uncertainty of the reaction rate calculated from the simulations. Note that due to an identical and nearly constant reactant concentration, the reaction rate is linearly proportional to the reaction rate constant.
Figure 5. Illustration of the simulation system containing a nanomotor. The simulation box is initially filled with blue monatomic fuel atoms. Red spheres represent inert atoms and green spheres represent catalyst atoms.
Figure 6. Motor positions as a function of time for five independent simulations. The initial temperature of the fuel is 116 K. The inset graph shows the distribution of the instantaneous velocity in the Y-direction of the motor for five independent simulations. The solid line is the best fit to a Maxwell-Boltzmann distribution plus a constant velocity of 5.6 m/s. The spread of the velocity distribution suggests a temperature of 171 K, which is within the temperature range of the fuel during simulations (from 116 to 186 K).
Figure 7. The formation of product molecules as described by the instantaneous position in the Y-direction and simulation time (black circles). The initial fuel temperature is 116 K. The two red lines denote the upper and lower edges of the nanomotor. The histogram of the reaction with respect to time is also shown (blue bars).
Figure 8

Average Kinetic Energy (eV) vs. Y-position (nm)

(a)
Figure 8. The spatial distribution along the Y-direction for the kinetic energy (a) and products (b) at different simulation times. The Y-position of each atom is shifted by the instantaneous position of the motor (lower edge). Therefore the nanomotor is stationary in this plot. The gray region denotes the motor position. Different simulation times are represented by black (380 ps), red (725 ps), green (1070 ps) to blue (1415ps) curves. Each curve is averaged over a time span of 70 ps from five independent simulations. Solid (broken) curves represent distributions among atoms that have X-Z projections within (outside) the nanomotor.
Figure 9. Top pane: the displacement of the motor for various initial fuel temperatures. Bottom pane: the amount of final products for various initial fuel temperatures. The onset of autonomous motion and chemical reaction coincide at about 80 K. The product counts for systems with high initial temperatures are out of the plot range.
Figure 10. The center of mass position of the unconstrained motors for five independent simulations. The arrows represent the driving direction of the motor (surface normal of the upper lid). The initial motor position is denoted by the solid oval at the bottom-right corner. The final motor positions are marked by the ovals with broken lines. Arrows with the same color belong to the same simulation. The size of the arrow is 0.3 nm.
Figure 11. Average velocities of the motor as a function of external forces. The initial fuel temperature is 116 K. The broken line is the best linear fit.
Figure 12. Motor thermodynamic efficiencies as a function of external loads. The solid line is calculated using Eq. (15).